

4

**MARKED UP VERSION**

Conventional solar cell technologies are based largely on single crystal, polycrystalline, or amorphous silicon. The source for single crystal silicon is highly purified and sliced into wafers from single-crystal ingots or is grown as thin crystalline sheets or ribbons. Polycrystalline cells are another alternative which is inherently less efficient than single crystal solar cells, but also cheaper to produce. Gallium arsenide cells are among the most efficient solar cells available today, with many other advantages, however, they are also expensive to manufacture.

In all cases of conventional solid-state photovoltaic cells, photon (light) absorption occurs in the semiconductor with both majority and minority charge carriers transported within the semiconductor; thus, both electron and hole transport must be allowed and the ~~band gap~~ band-gap must be sufficiently narrow to capture a large part of the visible spectrum yet wide enough to provide a practical cell voltage. For the solar spectrum the ideal ~~band-gap~~ band-gap has been calculated to be approximately 1.5 eV. Conventionally, expensive material and device structures are required to achieve cells that provide both high efficiency and low recombination probability and leakage.

Another class of conventional solar cells are the dye-sensitized photoelectrochemical solar cells as shown in Figure 2. These devices were derived from work on photoelectrochemical electron transfer and are cathode/electrolyte/anode systems in which a photoactive molecule is light activated and oxidized (or reduced) by electron (or hole) transfer to the adjacent semiconductor electrode. The charge transfer agents, which replace the transferred charge in the photoactive molecule, are typically molecules or atoms dissolved in a liquid electrolyte such that the molecules or atoms receive charges from an electrode. Reduction is performed by an electron donor in the liquid electrolyte. This device is limited in its power output by the relative free energies of electrons in the electrolyte and the semiconductor which limit the photovoltage. The maximum photovoltage is limited by the difference between the bottom of the conduction band edge and the liquid electrolyte chemical potential. Additional inefficiencies result from the required molecular diffusion of the donors to the electrode as well as overpotential losses at the electrode/electrolyte interface.

Another solid-state solar cell is the dye-sensitized Schottky barrier solar cell as described in U.S. patent nos. 4,105,470 and 4,190,950 by Dr. Skotheim. The Skotheim device is similar to the above-mentioned photoelectrochemical cell except the liquid electrolyte is replaced by a "reducing agent" layer, the property of which is not precisely identified in either the '470 nor the '950 patent. Purportedly, as a means of removing the band-gap restrictions of conventional PV's, an invention was reported by Skotheim who proposed a solid-state Schottky barrier device whereby a) photon absorption occurs in a photosensitive dye deposited on the surface of a semiconductor, b) majority charge carriers are injected directly into the conducting bands of the adjacent semiconductor, c) the ionized photosensitizer is neutralized by charges delivered by a reducing agent, d) a conductor provides charge to the reducing agent, and e) the Schottky barrier height will determine the device's ideal efficiency, and its height is determined by the interaction of the dye and the semiconductor. However, as previously mentioned, neither patent suggests the physical properties of the reducing agent, and it is unclear whether the proposed devices disclosed in the '470 and '950 patents can indeed yield the purported results. In the proposed cell

three separate molecular oxidation/reduction electron transfer steps are required (one from the excited dye to the adjacent semiconductor, one from the reducing agent to the dye, and one from the conductor to the reducing agent). Thus an electron must move from/to a conduction band to/from a molecular orbit twice and from one molecular orbit to another one. An implementation of the device was published using an organic hole transport material, however, the performance and longevity were poor [ref: U. Bach, et al., Nature, Vol. 395, October 1998, pg. 583-585].

The preferred embodiment of the present invention described herein is a multilayer solid-state structure wherein light absorption occurs in a photosensitive layer (molecules or nanostructures) and the energetic charge carriers produced by the absorption are transported ballistically, without significant energy loss, through an ultra-thin conductor, to and over an adjacent potential energy barrier that separates and stores the charge for use as electrical power. The potential energy barrier largely determines the device efficiency and can be optimized by choice of the device materials.

The essential components (e.g., layers) of the preferred embodiment of the present invention include: 1) a photosensitive layer where light energy is converted to electron and/or hole excitation, 2) an adjacent ultra-thin conducting layer that provides a pathway for ballistic transport of charges using high efficiency conduction bands, and as a source of replacement charges to the photosensitive layer[[]] and 3) a charge separation and collection layer such as an inorganic or organic semiconductor affixed with a back side ohmic contact opposite the ultra-thin conducting layer. The ohmic contact collects the charges transported across the barrier. The addition of an anti-reflection coating on top of the device is a highly practical embodiment of the invention.



The present invention is advantageous over the aforementioned dye-sensitized Schottky barrier solar cell structure in that it has the advantage of potentially greater photovoltages due to the ability to influence the barrier height by the choice of a high (for n-type semiconductors) or low (for p-type semiconductors) work function ~~conductors~~ conductor at the surface, by the choice of the semiconductor (type and doping level), and by the surface treatment of the semiconductor prior to disposition of the conductor to maximize the barrier height by affecting the interface. Additional advantages of the present invention include eliminating the need for a specific reducing agent or a minority charge carrier transport material, and providing the ability to choose from among a broad choice of charge separation layer material to include both wide band-gap n and p type semiconductors. In contrast to the prior art, U.S. patent nos. 4,105,470 and 4,190,950 by Skotheim, only two transfers of electrons to/from conduction bands are required and no inter-molecular charge transfer is necessarily required.

It is another object of the present invention to increase the efficiency of photovoltaic energy generation. More specifically, light absorption can be optimized since a single band-gap is not required for light absorption, and a large number and variety of materials with selectable spectral properties of photoabsorbing molecules or structures can be utilized without the need for compatibility with an electrolyte. Without the overpotential losses of the electrochemical redox reactions (both at the electrodes in the photoelectrochemical cell and by the reducing agent charge transfer), higher efficiencies are also possible. The ultra-thin conductor is used as an efficient ballistic transport channel and to maximize the photovoltage as determined by its effect on the barrier. The interaction between the conductor and charge separation layer to influence the barrier height, can be optimized by the choice of the conductor, charge separation material, and interface preparation.

The charge separation layer 39 is preferably made of a semiconductor material, or multiple semiconductors. Either inorganic semiconductor materials (e.g., titanium dioxide, zinc oxide, other metal and mixed metal oxides, moly sulfide, zinc sulfide, other metal and mixed metal sulfides, silicon carbide, etc.) or organic semiconductor materials, either hole conducting (e.g., triphenyldiamine (TPD), poly (p-phenylene vinylene) (PPV), poly (vinyl carbazole) (PVC), and their derivatives, etc.[]], or electron conducting (e.g., conjugated oligothiophenes, oxadiazole derivatives, etc.) may be used. In an alternative embodiment as shown in Figure 17, the charge separation layer 39 is made of an insulator or insulator-semiconductor composite structure with the key feature being alignment of the majority carrier bands with the absorber donor level (in Figure 3, 36 for n-type or in Figure 8, 84 for p-type). The ~~photosensitizer~~ photosensitive layer 10 can be a dye or any energy absorbing material or structure, and may include light absorbing atomic or molecular species on a surface (e.g., cis-di(thiocyanato)-N, N-bis-(2,2-bipyridyl-4,4-dicarboxylic acid)-Ru(II), phthalocyanines, carbocyanines, merbromin, 9-phenylxanthene, iron cyanate, etc.), or quantum structures (e.g., nanoparticles of CdS, CdSe, or

other semiconductors, or metals, or nanolayers of absorbing material). Additionally, multiple types and/or layers of different photoactive species can be used on the ~~photosensitizer~~ photosensitive layer 10 to maximize the spectrum capture of incident light. In an alternative embodiment, the photoactive species may be ~~imbedded~~ embedded in the front conductive layer to make a single composite layer.

In a specific fabrication example comprising the preferred embodiment of the invention, a charge separation layer 39 of titanium dioxide is deposited onto titanium foil (the ~~ohmic~~ back conducting layer ~~contact~~ 30). The charge separation layer 39 has a thickness ranging between 100 nm and 500 nm and is deposited by electron beam evaporation and/or by electroanodization of the titanium metal. Gold is then deposited to the composite layer to a thickness of 10 nm to form the ultra-thin conductor.

The operation of the preferred embodiment will now be discussed with reference to Figure 3. The preferred embodiment of Figure 3 produces electrical power from a photon energy source based on light energy conversion to charge excitation in a layer containing photosensitive molecules or structures. More specifically, a photon energy source 35 with energy  $h\nu$ , such as sunlight, is incident upon the photosensitive layer 10. The energy source excites electrons 36 located in the photosensitive layer 10 causing the electrons 36 to rise to a higher energy state. In accordance with the preferred embodiment, electrons having an energy level above the Schottky barrier height 25 (or slightly below if tunneling occurs) pass through the front conducting layer 31 via ballistic transport (ballistic transport refers to the transfer of electrons through a medium in which there is a low or zero scattering cross-section between the electrons and the medium through which they are transferred). The process of charge (electron) emission from the photoexcited absorber into and ballistically across the conduction bands of the conductor and charge separation layer is termed "Internal Charge Emission" .

Once the electrons travel through the front conducting layer 31, they travel through the charge separation layer 39 towards the back ohmic conducting layer 30 where they are stored with photon derived excess potential energy for later use (dissipation) in passing through the load 32. After losing their energy in the load 32 the electrons are returned to the front conducting layer 31. The maximum photovoltage of the device, or open circuit voltage, is determined by the potential barrier height between the front conducting layer 31 and the charge separation layer 39. In conventional Schottky solar cells (where the photons are absorbed in the semiconductor band-gap) the same maximum voltage is possible as determined by the barrier height. However ~~however~~, in the present invention the choice of semiconductors is not limited to those with solar spectrum absorbance. The voltage can be optimized or influenced by selecting appropriate materials for the front conducting layer 31 and the charge separation layer 39, and by specific treatments of the interface. For example, on clean silicon the Schottky barrier varies from approximately 0.4 eV to 0.8 eV as the conductor work function increases from approximately -2.5 eV (Ca) to -5.0 eV (Au) and on GaAs from 0.6 eV (for Mg) to 1 eV (for Pt). Preparation of the interface and metal can also be used to

increase the barrier for Pd on titanium dioxide where treatment of the metallic conductor Pd with oxygen causes an increase in the barrier of nearly 0.5 eV. The design approach is to maximize the barrier and still allow efficient carrier transport across the barrier and efficient replacement of photosensitizer (PS) charge by the conductor.



In accordance with an alternative embodiment, the charge separation layer 39 may be a thin insulating layer (PS-MIM configuration) wherein the conduction band edge and thickness of the insulator are chosen to allow charge carriers from the photoexcited state of the ~~photosensitizer~~ photosensitive 10 to move to the back contact and prevent current flow in the opposite direction.

In accordance with another alternative embodiment as shown in Figure 4, the ~~photosensitizer~~ photosensitive layer 10 is replaced with a layer of photoactive material 40 ~~comprising~~ comprised of clusters of atoms or molecules, including doped or quantum structures (quantum wells, nanoparticles, quantum dots, etc.), with dimensions engineered to maximize light absorbency and ballistic electron transfer. One advantage of this alternative embodiment is that the charged electrons transferred need not move into or out of an atomic or molecular system, which is the case when using a photosensitive dye. Rather, the electrons travel in and out of degenerate levels with less hindrance due to quantum state restrictions. A specific example would be the deposition of CdSe or CdS nanoparticles (~5 nm in dimension) on the conductor surface. These semiconductor particles have been shown to have efficient capture and efficient transfer to semiconductors. Interposing the conductor ballistic transport will still allow charge transfer; however, the ~~particle~~ particles can now be supplied with compensation charge directly from the conductor.

In accordance with another alternative embodiment of the present invention as shown in Figure 5, the electrons 36 of the ~~photosensitizer~~ photosensitive layer 10 do not ballistically transport through the front conducting layer 31. Rather, as the excited electrons 36 relax back to lower energy states, energy released from electrons 36 excites electrons 50 that reside in the front conducting layer 31. The excited electrons 50 may thereafter rise above the conduction energy band energy level 38 and flow towards the back conducting layer 30.

Figure 9 shows yet another alternative embodiment of the present invention wherein the charge separation layer 39 is made of a material having a narrow band-gap energy level (i.e., the conduction band energy level is close to the valence band energy level). The narrow band-gap property of the charge separation layer allows for excitation of additional electrons 90 from the underlying semiconductor material (as in a conventional Schottky diode solar cell). The internal emission supplements the photoexcitation of the ~~photosensitizer~~ photosensitive layer 10 and thereby produces additional energy.

Figure 11 shows a multilayer structure wherein multiple structures of the preferred embodiment as shown in Figure 3 ~~is~~ are deposited in a parallel fashion, separated by transparent spacer 112, to produce a superstructure that provides increased absorbency and efficiency in producing photovoltaic energy. Although Figure 11 shows a parallel combination of the preferred embodiment, it should be noted that a serial combination is also possible and feasible.

Figure 14 shows an embodiment where absorption occurs in a structure or molecule partially isolated from the conductor to reduce coupling for optimal charge transfer. Examples include metal oxides, silicon dioxide, titanium dioxide, aluminum dioxide, organic chains and self-assembled monolayers deposited on the surface prior to the photoabsorber. For example, a thin layer of titanium dioxide (~1-5 nm) is deposited on the conductor (Au). The photoactive merbromin is applied and forms a covalent linkage through its active carboxylate moiety to the titanium (C-O-Ti).

As previously discussed, in fabricating a device in accordance with the preferred embodiment, a charge separation layer 39 of titanium dioxide is deposited onto titanium foil (the ~~ohmic~~ back conducting layer ~~contact~~ 30). The charge separation layer 39 has a thickness ranging between 100 nm and 500 nm and is deposited by electron beam evaporation and/or by electroanodization of the titanium metal. Gold is then deposited to the composite layer to a thickness of 10 nm to form the ultra-thin conductor. The resulting current voltage curves of the Schottky contact are shown in Figure 18. Also shown in Figure 18 for comparison are devices using nickel instead of gold as the ultra-thin front conducting layer 31. An approximately 0.8 eV barrier results.

In accordance with the alternative embodiment of Figure 14, 2 nm of titanium dioxide is deposited onto the above-mentioned metal front conducting layer conductor 31 as a partial isolation layer. Photoactive merbromin is then applied and bonded covalently through its active carboxylate moiety to the titanium (C-O-Ti) to complete the active device.



Figure 15 shows an alternative embodiment comprising a polymer based device wherein a ballistic hole is injected into an ultra-thin hole carrier[[.]] : ~~Polymer~~ polymer A in Figure 15, (e.g., poly(p-phenylene vinylene), PPV) with its highest occupied molecular orbital (HOMO) level lower in energy than the HOMO of a second polymer (B in Figure 15) hole conductor layered behind it. The PPV provides a barrier to reverse hole transport serving the same role as the Schottky barrier. More traditional Schottky barrier devices have also been fabricated from polymer semiconductors and would be configured as in the above embodiments.